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| 6. AUTHOR(S)<br>R.M. Latanision, D.B. Mitton (MIT)<br>S.N. Lvov (Penn State)  |   |  |   |  |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>MIT 77 Mass Ave. Cambridge MA 02139<br>The Pennsylvania State University 206 Research East Building University Park, PA 16802   |   |  | 8. PERFORMING ORGANIZATION<br>REPORT NUMBER<br><br>-----<br>-----                       |  |
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| 13. ABSTRACT (Maximum 200 words)<br><br>There is a need both to destroy hazardous military and civilian waste and to identify safe and efficient alternative technologies. One effective process for the destruction of such waste is supercritical water oxidation (SCWO); however, materials degradation issues are one of the central challenges to this technology. It became apparent a number of years ago that maintaining a region thermodynamically favorable to alloy stability through feed stream modification could reduce degradation due to corrosion. However, a need for feedback from in-situ potential and pH electrodes was also recognized. This collaboration covered both the evaluation of corrosion phenomena in SCWO systems as well as the development of high temperature high pressure potential and pH electrodes for use in SCWO systems. Ultimately, the efficacy of feed chemistry control for SCWO systems was demonstrated during the project. |   |  |   |  |
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**Final Progress Report**

ARO Project Number: 41306-CH

Period Covered by Report: 1 August 2000 – 31 July 2003

Project Title: An Investigation of the Effect of Feed Chemistry Control by In-Situ Electrodes on Degradation in SCWO Environments

Contract or Grant Numbers: DAAD19-00-1-0446

Name of Institution: Massachusetts Institute of Technology  
Pennsylvania State University

Authors of Report: R.M. Latanision, D.B. Mitton (MIT)  
S.N. Lvov (PSU)

- (1) Foreword (optional)
- (2) Table of Contents (if report is more than 10 pages)
- (3) List of Appendixes, Illustrations and Tables (if applicable)
- (4) Statement of the problem studied

There is a need to destroy both military and civilian hazardous waste and an urgency, mandated by public concern over traditional waste handling methodologies, to identify safe and efficient alternative technologies. One effective process for the destruction of such waste is supercritical water oxidation (SCWO). By capitalizing on the properties of water above its critical point (374 °C and 22.4 MPa for pure water), this technology provides rapid and complete oxidation with high destruction efficiencies at typical operating temperatures. Although SCWO is demonstrably capable of destroying hazardous wastes, the process must be carried out in a reactor capable of accommodating elevated temperatures, pressures, and degradation problems that may result from aggressive feed streams<sup>1-4</sup>. A recognition of materials degradation as one of the central challenges to the ultimate commercialization of this technology has precipitated a number of potential methodologies for corrosion mitigation, including: (i) corrosion-resistant liners and coatings, (ii) reactor design and (iii) feed stream modification. It has become apparent that an oxidizing potential-pH region exists within which thermodynamic conditions favor the formation of insoluble Cr, Ni, and Fe. Maintaining this thermodynamic region through feed stream modification controlled by feedback from in-situ potential and pH electrodes could reduce degradation due to corrosion for alloys containing these elements. On the other hand, the accurate measurement of potential and pH in a high temperature aqueous solution still remains a challenge for experimental studies of the corrosion processes in the SCWO environment. Earlier experimental research at PSU focused on the development and fabrication of electrochemical sensors and systems to measure the potential and pH in high temperature sub- and supercritical aqueous systems.

**(5) Summary of the most important results**

A number of years ago<sup>5</sup> we proposed that use of judicious feed modification during waste destruction in SCWO systems as a potential methodology to reduce corrosion by achieving favorable thermodynamics. It was postulated that this would permit the use of conventional alloys during fabrication as opposed to the use of less typical materials such as platinum. The primary objectives for this project were: (i) to assess the potential for corrosion mitigation through feed modification controlled by in-situ electrodes, and (ii) to develop a monitoring methodology applicable to the SCWO environment.

The experimental configuration presented in Figure 1 was employed to assess a number of high nickel alloy wire samples.

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In use, the orientation of the experimental apparatus is vertical; however it is shown here in the horizontal configuration for ease of presentation. The autoclave shown in this figure, is based on a 3/8 inch OD alloy 625 thick-walled vertical vessel with "Hi-Pressure Inc" fittings at both ends. Thermocouples were semi-permanently attached at intervals along the external wall to permit correlation of temperature and corrosion, which has previously been shown to be significant<sup>5,7</sup>.

During each individual test, the wire sample was exposed to HCl with an ambient pH of 2 at a pressure of approximately 24.1 MPa, and both sub- and supercritical temperatures. Subsequent to an experiment samples were mounted and examined both analytically and metallographically.

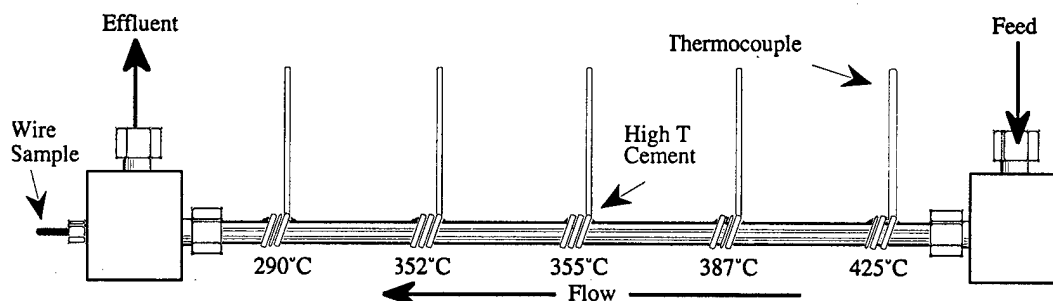


Figure 1 - The experimental configuration employed for assessing wire samples over an extensive temperature range. A similar design, excluding the wire sample and fitting, was also used for assessing tube samples.

Figure 2 reveals one of the corrosion phenomena that is commonly observed in supercritical systems incorporating simple (non-salt forming) feeds. There is a maximum in the depth of penetration at a high subcritical temperature, and the degradation decreases above the critical point.

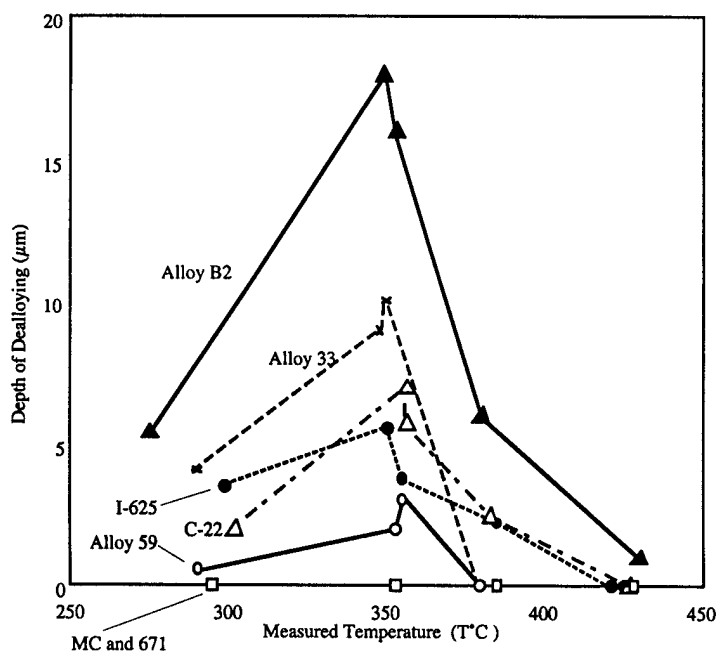


Figure 2 - The depth of dealloying as a function of temperature for various high nickel alloys exposed to an acidic chlorinated feed stream.

As presented in Figure 2, this trend is apparent for all of the high nickel alloys tested except for the MC alloy and alloy 671, which exhibit essentially no corrosion.

A phenomenological approach has been adopted to explain the decrease in corrosion in the near critical region<sup>8</sup>. This treatment of the subject considers  $H^+$  and  $O_2$  as the only aggressive species, and Cl induced localized attack is not considered. By calculating the relative corrosion rate (based on changes in the hydrogen ion concentration and the density of water as a function of temperature) over the temperature range associated with SCWO systems, an increase with increasing temperature is observed until a maximum is reached as the critical point is approached. With a further increase in temperature, the relative corrosion rate decreases. This decrease is associated with a rapid reduction in the concentration of aggressive species as a function of an increasing supercritical temperature. The reduction in aggressive species reflects the combined effect of the decrease in the dissociation constant, resulting in a decrease in acid dissociation, and the decrease in the solution density.

While this is now a familiar occurrence, it is essential to consider other contributory phenomena not strictly related to changes in the solution. Figure 3 presents an SEM micrograph of an alloy 625 tube sample that was exposed at 24.1 MPa to an acidic chlorinated feed at a supercritical temperature. Exposure was discontinuous, generally in 24 hour periods, with a total accumulated time of approximately 210 hours. This sample reveals cracking at a temperature (425°C) that is substantially above the critical point. However, between individual exposure periods the sample was exposed to 15MΩ deionized water during cooldown and heatup. These temperature excursions included a range of temperatures from supercritical to ambient. As a result, it is not possible to define precisely the conditions that precipitated the crack development. On the other hand, as this situation closely reproduces the conditions that would be experienced by a SCWO facility during operation, the potential for crack development within all temperature regions, including supercritical, needs to be recognized. Cracking of both alloy 625 and alloy C-276 has previously been reported at supercritical temperatures after extended exposure times<sup>1</sup> on the order of 300 hours.



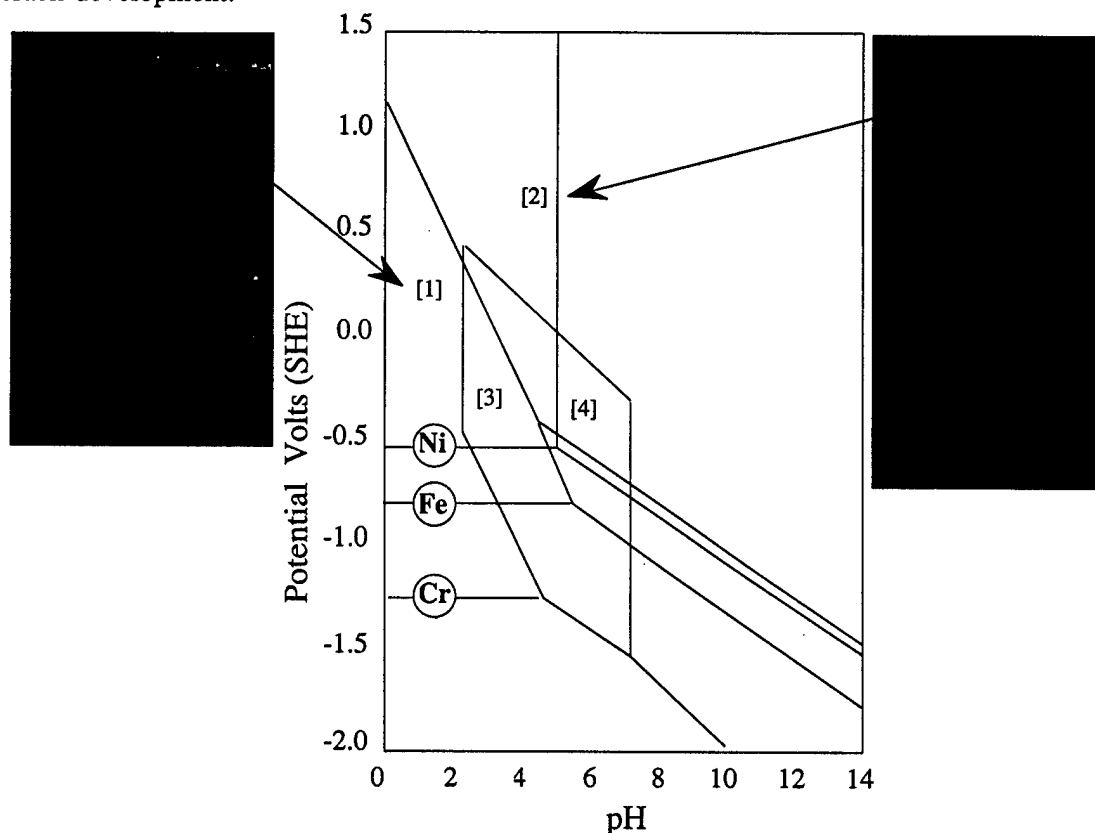
**Figure 3** - SEM micrograph of an alloy 625 tube exposed discontinuously at 425°C for a total of approximately 210 hours to an HCl feed stream with an ambient pH of 2.

Experiments incorporating a high temperature electrochemical cell<sup>9</sup> were carried out at Penn State University with alloy C-276 tube samples. The flow-through YSZ electrode has been redesigned to

allow in-situ pH measurements of high temperature solutions in a manner similar to that commonly used for pH measurements at ambient conditions. The new design has significantly reduced the failure rate of the electrode due to YSZ tube breakage. During an experiment, the temperature and pressure were maintained at 350°C and 27.3 MPa, respectively. The experiment duration was either 53 or 70 hours,

and the potential and pH were monitored in-situ. Subsequent to a test, samples were mounted and metallographically and analytically assessed at MIT.

Figure 4 presents the superimposed E-pH diagrams for Ni, Cr and Fe at 300°C in conjunction with the SEM micrographs representative of the sample morphology subsequent to a test in a chlorinated feed stream. For the more acidic conditions indicated by [1] in this figure, the in-situ pH at 350°C was 0.48, and the test was conducted for 53 hours. The sample exhibits severe cracking around the periphery. For the less acidic condition [2], the in-situ pH at 350°C was 4.4, and the test was conducted for 70 hours. This sample revealed negligible degradation and there was no indication of any crack development.



**Figure 4** The superimposed E-pH diagrams for Ni, Cr and Fe at 300°C in combination with the SEM micrographs representative of sample morphology for the test conditions.

We have previously reported results for a failure analysis conducted on an alloy C-276 preheater tube<sup>5</sup> exposed to a high subcritical temperature. The approximate conditions that the failed preheater tube experienced are represented by [3] in Figure 4. In addition to cracking, the preheater tube exhibited preferential loss of nickel and iron; however, chromium was stable. It was possible to reproduce both the dealloying and cracking by exposing an identical tube to an HCl feed with an ambient pH of 2. In this case<sup>6</sup>, the tube exhibited essentially no corrosion above the critical point; however, severe cracking was observed at a high subcritical temperature. These and similar experiments suggested the possibility of feed chemistry control to reduce degradation. The general region designated by [4] in Figure 4 was considered to be the preferred region within which corrosion would be minimized as a result of the thermodynamic stability of some of the main alloying elements for high nickel alloys.

While it is likely that achieving the conditions associated with [4] in Figure 4, would improve the life of a SCWO system, there was some concern regarding the effect that reducing the oxidizing potential would have on the destruction efficiency, and the need to extend reactor residence times was considered possible. As apparent in Figure 4 however, even for more acidic and substantially more oxidizing conditions, the kinetics of degradation are substantially reduced. While continued research is necessary, these results demonstrate the efficacy of feed chemistry control for SCWO systems.

**(6) Listing of all publications and technical reports supported under this grant or contract.**

**Provide the list with the following breakout, and in standard format showing authors, title, journal, issue, and date.**

**(a) Papers published in peer-reviewed journals**

D.B. Mitton, N. Eliaz, J.A. Cline and R.M. Latanision: *An Overview of the Current Understanding of Corrosion in SCWO Systems for the Destruction of Hazardous Waste Products*, Mat. Tech. and Adv. Perf. Mat., Vol. 16, p. 44 (2001).

Lvov S.N., Zhou X.Y., Fedkin M.V., Zhou Z., Kathuria A., and Barnes H.L. Advanced Electrochemical Studies of Hydrothermal Systems, *Geochimica et Cosmochimica Acta*, v. 66, p. A467 (2002).

Lvov S. N., Zhou X. Y., Ulmer G. C., Barnes H. L., Macdonald D. D., Ulyanov S. M., Benning L. G., Grandstaff D. E., Manna M., and Vicenzi E. Progress on yttria-stabilized zirconia electrodes for hydrothermal pH measurements, *Chemical Geology*, **198**, 2003, 141-162.

Seneviratne D.S., Papangelakis V.G., Zhou X.Y., Lvov S.N., Potentiometric pH measurements in acidic sulfate solutions at 250 degrees C relevant to pressure leaching, *Hydrometallurgy*, **68**, 2003, 131-139.

Zhou X.Y., Zhou Z.F., Bundura A., Lvov S.N. Potentiometric Measurements of the Association Constant of HCl(aq) in High Subcritical and Supercritical Temperatures up to 400°C" (submitted to *Journal of Supercritical Fluids*).

**(b) Papers published in non-peer-reviewed journals or in conference proceedings**

R.M. Latanision, D.B. Mitton and N. Eliaz: Stress Corrosion Cracking in Supercritical Water Systems for Waste Destruction, *Proceedings of the TMS Symposium in Honor of R.W. Staehle*, New Orleans, LA, Feb. 11-15 (2001).

D.B. Mitton, N. Eliaz, J.A. Cline and R.M. Latanision: Assessing Degradation Mechanisms in Supercritical Water Oxidation Systems, Paper 352, *Corrosion 01*, Houston, TX, Mar. 11-16 (2001).

J.A. Cline, P.A. Marrone, J.W. Tester, D.B. Mitton and R.M. Latanision: *Corrosion Mechanisms in N10276 in Hydrothermal HCl Solutions*, Paper 362, *Corrosion 01*, Houston, TX, Mar. 11-16 (2001)

D. B. Mitton, H. Kim, J. Zhang and R. M. Latanision: An Examination of Degradation Modes of Constructional Materials for Supercritical Water Oxidation System Fabrication, *Proc. of the 2002 Tri-Service Corrosion Conference*, San Antonio, TX, Jan. 14-18 (2002).

D.B. Mitton, H. Kim, J. Zhang, N. Eliaz, C.R. Sydnor and R.M. Latanision: An Examination of the Corrosion Phenomena of Potential Constructional Materials for SCWO System Fabrication, Paper 353, *Corrosion 02*, Denver, CO, Apr. 7-12 (2002).

Lvov S.N. Advanced Electrochemical Technique for Hydrothermal Systems, In: The Proceeding of 5<sup>th</sup> International Conference on Solvo-Thermal Reactions. Ed. Riman R.E., ICSTR, East Brunswick, NJ, 2002, 1-6.

R.M. Latanision and D.B. Mitton: Corrosion Phenomena of Potential Materials for Fabrication of SCWO Systems, Proc. 15th ICC, Granada, Spain, Sept. 22-27 (2002).

(c) Papers presented at meetings, but not published in conference proceedings

(d) Manuscripts submitted, but not published

(e) Technical reports submitted to ARO

(7) List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project

PI's

R.M. Latanision (MIT)

S.N. Lvov (PSU)

D.B. Mitton (MIT)

Graduate Students

H.-J. Kim (PhD - MIT)

C. Sydnor (Masters - MIT)

S. Ulyanov (PhD - PSU)

A.J. Thomas (Masters - PSU)

Postdoctoral

J. Zhang (MIT)

N. Eliaz (MIT)

X.Y. Zhou (PSU)

Z.F. Zhou (PSU)

(8) Report of Inventions (by title only)

Yttria-Stabilized Zirconia Membrane Electrode, X.Y. Zhou, S.N. Lvov, S.M. Ulyanov, US Patent No 6,517,694, 11 February 2003.

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3. D.B. Mitton, J.H. Yoon, J.A. Cline, H.S. Kim, N. Eliaz and R.M. Latanision: The Corrosion Behavior of Nickel-Base Alloys in SCWO Systems, *Ind. Eng. Chem. Research*, Vol. 39, p. 4689 (2000).
4. R.M. Latanision and D.B. Mitton: Stress Corrosion Cracking in Supercritical Water Systems, *Proceedings of the 1st Int. Symp. on Supercritical Water-Cooled Reactors, Design and Technology (SCR-2000)*, Tokyo, Japan, Nov. 6-9 (2000).
5. D.B. Mitton, P.A. Marrone and R.M. Latanision, " Interpretation of the Rationale for Feed Modification in SCWO Systems", *J. Electrochem Soc.*, Vol. 143, 1996, p. L59.
6. D.B. Mitton, S.H. Zhang, M.S. Quintana, J.A. Cline, N. Caputy, P.A. Marrone and R.M. Latanision, "Corrosion Mitigation in SCWO Systems for Hazardous Waste Disposal", *The Symposium on Corrosion in Supercritical Fluids, Corrosion 98*, 1998, Paper 414.
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8. L.B. Kriksunov and D.D. Macdonald, "Corrosion in Supercritical Water Oxidation Systems: A Phenomenological Analysis", *J. Electrochem. Soc.*, 142 (12), 1995 , p. 4069.
9. S.N. Lvov, G. C. Ulmer, X. Y. Zhou, H.L. Barnes, D.D. Macdonald, S.M. Ulyanov, L. G. Benning, D. E. Grandstaff, M. Manna, and E. Vicenzi, "Electrochemistry and Structure of Yttria-Stabilized Zirconia Sensors for Hydrothermal pH Measurements," *Chemical Geology*, 2002 (in press)

#### **(10) Appendixes**